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Chemical Studies on the Ocean. (LXII)

On the Amount of Cesium dissolved in Sea-water

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Investigation was made in order to determine the amount of cesium dissolved in sea water. Cesium was coprecipitated with K and Rb as cobaltinitrates; after removal of Co, their dipicrylaminates were precipitated and by the treatment with acetone and HCl, chlorides were obtained. The greater part of KCl was removed by Wells-Steven's method and the residual chlorides were changed into nitrates. Then, Rb and Cs were precipitated using Ball's reagent containing AgNO_3 . After removal of Ag and Bi, the sum of Rb and Cs estimated as dipicrylaminates. Cesium was precipitated with iodobismuthic acid and determined by measuring the amount of Bi in the precipitate. The recovery of Cs was measured by using Cs^{137} as tracer. 3~4 γ of Cs per liter of sea waters sampled at Suma, Koganoura and Shirahama has been found.

A new method has been established for the indirect determination of small amount of cesium in the presence of a large amount of rubidium, based upon the precipitation of cesium as $\text{Cs}_3\text{Bi}_2\text{I}_9$, followed by photometric determination of bismuth (6) with the correction by the measurement of recovery efficiency with a radiometric tracer. The procedure under the conditions used is accurate to about $\pm 20\%$. This method was applied to sea water, and 3.4~4.3 γ of cesium was found in a liter.

Determination of Small Amount of Cesium

It was previously reported that the composition of the cesium compound precipitated with KBiI_4 reagent in conc. acetic acid was $\text{Cs}_3\text{Bi}_2\text{I}_9$ (3) and the amount of coprecipitated rubidium was nearly constant or gradually changed at a certain range of rubidium (4). These facts have been applied to the determination of trace amount of cesium in the presence of potassium and rubidium.

REAGENT AND APPARATUS

Iodobismuthic Acid: 4 g. of purified bismuth trioxide was dissolved in the hydroiodic acid which was obtained by passing hydrogen sulfide gas into 100 ml. of water containing 20 g. of purified iodine. The filtered solution in a glass-stoppered

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bottle was stored in a cold place avoiding light. It holds the use for about three months.

Dithizone-Chloroform Solution: 60 mg. of dithizone was dissolved in dilute ammonium hydroxide solution (1 : 200) and impurities were extracted with chloroform. The aqueous dithizone phase was filtered through a pledget of cotton inserted in the stem of a separatory funnel into another funnel. The filtrate was carefully acidified with metal-free hydrochloric acid (1 : 1) to precipitate dithizone, which was then reextracted into purified chloroform. The chloroform layer was filtered as before and diluted to 500 ml. with purified chloroform for use.

Rubidium Chloride: The rubidium chloride was purified by our method (5). The cesium which might be present in a very little quantity in the rubidium chloride, was not identified with iodobismuthic acid which was capable of detecting as little as 0.2 γ of cesium. Moreover, it was confirmed that there were no interferences even in the determinations of cesium in large amounts of rubidium.

Nitric Acid: 1 % and 3 % solutions.

Concentrated Ammonium Hydroxide: Redistilled.

Potassium Cyanide: Special grade reagent.

A Hitachi filter photometer Model EPO-A equipped with 1-cm. cells and filters of approximately 30 m μ band width was used for all photometric measurements. A Beckman Model H-2 pH meter was utilized to measure the pH values and a GM counter was used for the measurement of radio-activity.

The glass apparatus as illustrated in Fig. 1 was used. (A) is a graduated 10 ml. vessel and (B) a filter-stick with a sintered glass-filter-plate.

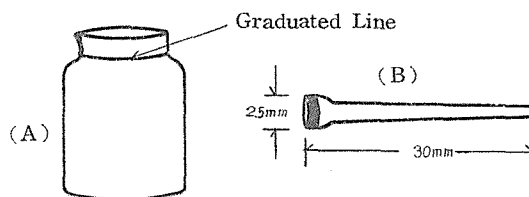


Fig. 1. Glass apparatus.

PROCEDURE

The sample containing a small amount of cesium is taken in the vessel shown in Fig. 1 and evaporated to dryness on a steam-bath. After drying the residue in an air-bath at about 150°C for an hour, it is cooled in a desiccator. Then, three drops (0.03~0.04 ml.) of iodobismuthic acid which has been cooled in an ice-water for more than an hour is added to the ice-cooled vessel and the vessel is moved so as to wet the vessel wall with reagent. As soon as the other salts accompanied with cesium—generally, potassium and rubidium salts have dissolved, the precipitate

is filtered through the filter-stick. This operation is generally done in 4 mins. after the addition of reagent, and is satisfactory even in the presence of 4 mg. of potassium or rubidium. The precipitate is washed with 1 ml. of cold conc. acetic acid five to six times and treated with 3 ml. of 3 % nitric acid. After heating it on a steam-bath for about 30 min., the filter-stick is washed with 1 % hot nitric acid and the filtrate is received in the previous vessel. The solution is transferred into a separatory funnel and the iodine which may remain is removed with 10 ml. of chloroform. Then 20 ml. of potassium cyanide-ammonium hydroxide solution (10 gr. KCN/1 litre NH_4OH), 40 ml. of 1 % nitric acid which has been treated with 8 ml. of dithizone-chloroform solution, and exact 15 ml. of dithizone-chloroform solution are added to the solution. After shaking for about 1 min., the chloroform layer is filtered through a filter paper and the absorbance is read comparing with a blank throughout the analysis.

RESULTS

Calibration curve for cesium obtained by means of the above mentioned procedure is shown in Fig. 2. It was found that in the absence of interfering ions, the Beer's law holds for the concentration range of 2.3 to 45 γ of cesium per 15 ml..

Determination of Cesium in the Presence of Potassium

The results obtained in the presence of potassium are shown in Table 1. Up to 4000 γ , potassium does not interfere for the determination of 10~45 γ of cesium, but in the presence of potassium more than 2000 γ , the evaluations of cesium less than 10 γ give negative errors owing to the salt effect.

Table 1. Determination of Cesium in the Presence of Potassium

K present γ	Cs taken γ	Cs found γ	Error γ	K present γ	Cs taken γ	Cs found γ	Errors γ
10	2.5	2.3	-0.2	2000	2.5	2.0	-0.5
	5	4.3	-0.7		5	4.6	-0.4
	10	11.5	+1.5		10	8.7	-1.3
	15	14.1	-0.9		15	14.0	-1.0
	25	24.7	-0.3		25	26.3	+1.3
	35	33.2	-1.8		35	33.7	-1.3
	45	46.4	+1.4		45	47.1	+2.1
100	2.5	2.4	-0.1	4000	2.5	1.2	-1.3
	5	4.6	-0.4		5	2.6	-2.4
	10	9.1	-0.9		10	7.8	-2.2
	15	13.8	-1.2		15	14.1	-0.9
	25	26.5	+1.5		25	26.2	+1.2
	35	34.8	-0.2		35	33.6	-1.4
	45	43.3	-1.7		45	42.2	-2.8

Determination of Cesium in the Presence of Rubidium

The results obtained in the presence of rubidium are shown in Table 2, and the relations between the absorbance and the amount of existing rubidium are given in Table 3. for various amounts of cesium.

Table 2. Determination of Cesium in the Presence of Rubidium.

Cs taken γ	Rb taken γ	Cs found γ	Error γ	Cs taken γ	Rb taken γ	Cs found γ	Error γ
2.5	2.5	2.25	-0.25	2.5	10	2.75	+0.25
5	5	4.5	-0.5	5	15	5.0	± 0
10	10	9.5	-0.5	10	20	9.5	-0.5
15	15	15.6	+0.6	15	30	16.75	+1.75
25	25	23.0	-2.0	25	50	30.25	+5.25
35	35	37.5	+2.5	35	70	44.0	+9.0
45	45	49.3	-4.3	45	90	—	very positive

As can be seen from Table 2, it is obvious that the calibration curve (Fig. 2) can be used in the presence of rubidium less than cesium, but it cannot be used in the presence of rubidium more than cesium, that is to say, the found values of cesium involve large positive errors with increasing amount of rubidium. These results correspond to those obtained in the gravimetric analysis of semi-micro quantities of cesium (3,4).

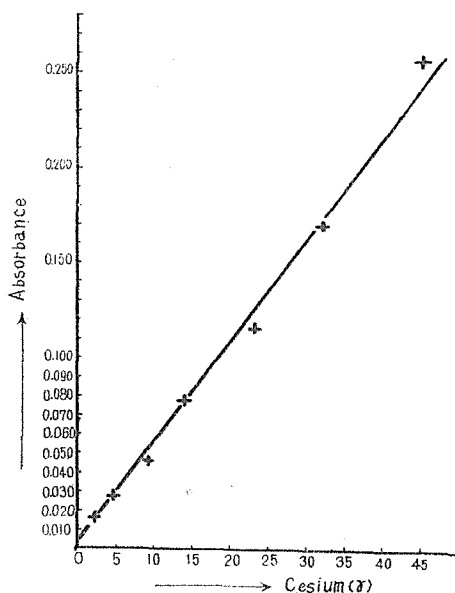


Fig. 2. Calibration curve for Cesium.

However, it is well shown in Table 3 that absorbances change only gradually

Table 3. Relation between Absorbance and Content of Rubidium.

Cs taken	Rb taken	Absorbance	Cs taken γ	Rb taken γ	Absorbance
2.3	0	0.061	2.5	2.5	0.015
4.6	0	0.026	5	5	0.026
9.2	0	0.045	10	10	0.052
13.8	0	0.079	15	15	0.082
23.0	0	0.115	25		0.121
32.0	0	0.168	35	35	0.197
45.0	0	0.255	45	45	0.298
2.5	10	0.017	2.5	50	0.013
5	15	0.027	5	50	0.021
10	20	0.052	10	50	0.057
15	30	0.088	15	50	0.093
25	50	0.159	25	100	0.150
35	70	0.245	35	100	0.230
45	90	0.364	45	100	0.383
10	500	0.053	10	750	0.051
15	500	0.105	15	750	0.097
25	500	0.158	25	750	0.169
35	500	0.233	35	750	0.255
45	500	0.398	45	750	0.413
10	1000	0.045	10	1500	0.041
15	1000	1.091	15	1500	0.082
25	1000	0.182	25	1500	0.193
35	1000	0.277	35	1500	0.293
45	1000	0.437	45	1500	0.456
10	2000	0.038	10	2500	0.035
15	2000	0.076	15	2500	0.081
25	2000	0.206	25	2500	0.217
35	2000	0.328	35	2500	0.335
45	2000	0.480	45	2500	0.496
10	3000	0.033	10	3500	0.032
15	3000	0.074	15	3500	0.081
25	3000	0.234	25	3500	0.241
35	3000	0.348	35	3500	0.356
45	3000	0.508	45	3500	0.522
10	4000	0.030			
15	4000	0.083			
25	4000	0.250			
35	4000	0.369			
45	4000	0.536			

with the increase of rubidium, and good values can be obtained if we take the following groups with regard to the rubidium and use the calibration curve within its respective range of rubidium: $0 \sim X$, $X \sim X+500$, $X+500 \sim X+1000$, $X+1000 \sim X+1500$ γ etc. — here X denotes the amount of rubidium equal to cesium contained in a sample.

As a preliminary experiment for the determination of cesium dissolved in sea water, a measurement was made for the samples containing 2000 γ of rubidium and each 10, 20, 30 γ of cesium. The sum of rubidium and cesium was found by the conventional method (7) in which rubidium and cesium were weighed as their dipicrylamines (H_{Rb+Cs}). After removal of amine, the amounts of cesium were determined by the above-mentioned procedure using the calibration curve obtained in the presence of 2000 γ of rubidium. The results are shown in Table 4.

Table 4. Determination of Cesium in the Presence of a Large Amount of Rubidium.

		I	II	III
Cs taken	γ	10	20	30
Rb taken	γ	2000	2000	2000
H_{Rb+Cs}	mg	12.10	12.23	12.35
$Rb(\rightleftharpoons Rb+Cs)$	γ	1976	1997	2017
Absorbance		0.032	0.161	0.229
Cs found	γ	9.2	21.75	27.25
Error	γ	-0.8	+1.75	-2.75

According to the results, the interferences by the presence of potassium and rubidium were almost analogous to that case of rubidium alone. Thus, a small amount of cesium in potassium, rubidium and their mixture can be easily estimated without separating it; we may only take into account of the interferences of rubidium.

Determination of Cesium dissolved in Sea-water

As for the amount of cesium dissolving in sea water, we cannot find good data, and some values (2 γ /l (1), $2 \sim 10 \times 10^{-3}$ γ /l (2)) of cesium given by several authors are remarkably different from one another, and moreover, they seem to be inadequate.

REAGENTS

Sodium Cobaltinitrite: 50 gr. of $Co(NO_3)_2 \cdot 6H_2O$ and 110 gr. of $NaNO_2$ are dissolved in 300 ml. of water and 40 ml. of 50 % acetic acid is added. After removal of nitrogen oxide gas under sucking for 12 hrs., the solution is filtered.

Dipicrylamine (H_R): The H_R precipitated in a slight alkaline solution is dissolved in a minimum amount of acetone. The amine precipitated with nitric acid

is digested in hot water, filtered and washed.

Reagent A: 9N NaNO_2 solution.

Reagent B: 20.5 gr. of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 2 gr. of AgNO_3 are dissolved in 100 ml. of 6N acetic acid. The solution is filtered through a glass-filter.

Reagent C: A mixture of 3 parts of reagent A and 2 parts of reagent B.

Cs^{137} Standard Solution: The Cs^{137} in the form of Cs^{137}Cl solution was obtained as processed isotope from the U.S. Atomic Energy Commission, Isotopes Division, Oak Ridge, Tenn. Twenty mg. of ammonium chloride, excess perchloric acid, and $\text{C}_2\text{H}_5\text{OH}$ are added to 50 ml. of the solution which is obtained by dilution of 0.7 ml. of original solution to a litre — here 1 ml. corresponds to approximately $1\ \mu\text{C}$. $\text{Cs}^{137}\text{ClO}_4$ obtained by precipitation with ammonium perchlorate is dissolved in hot water and diluted to 25 ml. with distilled water. One ml. of the solution has nearly the strength of $2\ \mu\text{C}$. The mass of Cs^{137} which has the strength of $2\ \mu\text{C}$., is theoretically computed with the following formula:

$$M = 3.7 \times 10^7 \times 1.44 T(W/N) \times 2 \times 10^{-3} = 0.02828\ \gamma.$$

Where, M = mass of the radioactive isotope which has the strength of $2\ \mu\text{C}$. (γ)

W = atomic weight

T = half-life (sec.)

N = Avogadro's number (6.02×10^{23}).

This convinces us that our farther experiments will be free from any disturbance due to the mass of Cs^{137} .

PROCEDURE

To the 10 litres of sea water in a small necked bottle 1 ml. of the Cs^{137} standard solution and 200 ml. of $\text{Na}_2\text{Co}(\text{NO}_2)_6$ reagent are added. In about 3 hrs., the produced cobaltinitrites of K, Rb and Cs completely fall down to the bottom and the supernatant liquid is siphoned out as much as possible. It was already reported that under the above conditions, if the temperature of solution was below 10°C , small amount of Rb and Cs in solution was quantitatively precipitated, but with the ascent of temperature the recovery of Rb and Cs decreased remarkably (10). The precipitates are transferred into a beaker and dissolved by heating with 4 ml. of conc. H_2SO_4 . Then Co is removed as a hydroxide and it is reprecipitated. H_H is added to the hot filtrate, and after cooling H_K , H_{Rb} and H_{Cs} are obtained by means of the conventional method. After removal of H_H , the filtrate is evaporated until a crystal deposits on the vessel wall. Then, the deposited KCl is filtered off and washed with conc. HCl. The filtrate is evaporated to the same volume as before, filtered and washed with $\text{HCl}-\text{C}_2\text{H}_5\text{OH}$ (1:1) solution. The filtrate is heated for some time, filtered after cooling and washed with $\text{HCl}-\text{C}_2\text{H}_5\text{OH}$ (1:2) solution. Thus the most part of KCl is removed from Rb and Cs. The chlorides are

converted into the nitrates with nitric acid (8). The nitrates free from nitric acid are dissolved in 4 ml. of water, and, 3 ml. of reagent A and 2 ml. of reagent B are added. After ice-cooling for 2 hrs., the precipitates are washed 5 to 6 times with each 0.8 ml. of the ice-cooled reagent C. The precipitates are recrystallized and dissolved with dil. HNO_3 . Though the separations of Rb and Cs from K could be done quantitatively by these operations (9), the details of procedure are not reported in this paper. With a few drops of 6*N* HCl and H_2S , Ag and Bi are precipitated. After vaporization of the filtrate to dryness, the sum of Rb and Cs is found using 0.1*N* H_2O_2 reagent. The filtrate which is obtained by removal of the amine, is diluted to the mark of the vessel shown in Fig. 1 (A) and an activity of the solution is measured by a GM counter. By comparison with that of the Cs^{137} standard solution under the same conditions, an efficient recovery of Cs is found. After measurement of Cs by the mentioned procedure first, the true amount of Cs dissolved in sea water is obtained with a correction based upon the recovery.

RESULTS

The sea waters were sampled at Suma, Hyogo Pref., Koganoura and 6 miles in the west of Shirahama, Wakayama Pref., in March 1953.

Table 5. Surface Sea Water at Suma.

		I	II	III
Sea Water	l	10	10	10
Chlorinity	%	17.64	17.64	17.64
Solution Temp.	°C	11	11	11
$\text{Na}_3\text{Co}(\text{NO}_2)_6$	ml.	200	200	200
$\text{H}_{\text{Rb}+\text{Cs}}$	γ	13650	14280	12800
Rb found	γ	2230	2320	2090
Recovery	%	85.0	89.1	82.9
Cs found	γ	36	33	30
Cs in Sea Water	γ/l	4.1	3.6	3.5

Table 6. Sea Water at Koganoura and 6 Miles in the West of Shirahama.

No.	Shirahama			Koganoura	
	I	II	III	IV	
Depth from Surface	m.	5	20	45	5
Chlorinity	%	18.48	18.61	18.99	18.22
Solution Temp.	°C	13.5	13.5	13.5	13.5
Na ₃ Co(NO ₂) ₆	ml.	200	200	200	200
H _{Rb+Cs}	γ	16910	18600	14530	14010
Rb found	γ	2760	3040	2370	2290
Recovery	%	72.3	73.0	75.1	82.5
Cs found	γ	27	32	35	30
Cs in Sea Water	γ/l	3.4	4.1	4.3	3.5

The results are shown in Table 5 and 6 respectively.

In these experiments, the recovery was a little low owing to the fact that the sea water was treated on the spot and solution temperature was higher than 10°C. So the found amounts of Rb were lower than true values. On the amounts of Rb dissolved in sea water, it has been already reported (10).

Determination of Cesium dissolved in Brine

Rb and Cs were directly precipitated with an excess H_4 from 2 litres of brine, and the amounts were found by the same procedure as shown in Table 7.

Table 7. Analysis of Brine.

Brine taken	1	2
sp. gr. of Brine		1.12
H_{Rb+Cs}	γ	9900
Rb found	γ	1620
Recovery	%	77
Cs found	γ	17.5
Cs in Brine	γ/l	8.8

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REFERENCES

- (1) H. Wattenberg, *Z. anorg. allgem. Chem.*, **236**, 339 (1938);
H. Wattenberg, *Z. anorg. allgem. Chem.*, **251**, 86 (1943).
- (2) M. Ishibashi and Y. Harada, *J. Chem. Soc. Japan*, **64**, 1049 (1943).
- (3) Read at the meeting of Kinki Division, Chem. Soc. of Japan, March 1950.
- (4) Read at the Fourth Annual Congress, Chem. Soc. of Japan, April, 1950.
- (5) Read at the meeting of Kinki Division, Chem. Soc. of Japan, February 1950.
- (6) D. M. Hubbard, *Anal. Chem.*, **20**, 363 (1948);
E. P. Laug, *Anal. Chem.*, **21**, 188 (1949).
- (7) I. M. Kolthoff and G. H. Bendix, *Ind. Eng. Chem., Anal. Ed.*, **11**, 94 (1939);
S. Sato, *J. Chem. Soc. Japan*, **72**, 182 (1951).
- (8) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis" p. 117, New York, John Wiley & Sons, 1929.
- (9) Read at the First Annual Congress, Japan Society for Analytical Chemistry, October 1951 under the title of "Chemical Studies on the Rare Alkali Elements" (Part 9).
- (10) Ditto, "Chemical Studies on the Rare Alkali Elements" (Part 10).